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13. ABSTRACT *(Maximum 200 words)*

Ion beam fabrication techniques have been used to form a wide range of elemental metal nanocrystals in high purity dielectrics. Implantation protocols and post processing treatments have been established to control the size and size distribution of the elemental nanocrystals. This control has allowed us to correlate the nanocrystal microstructure with the optical response and to show that the quantum size effects are present and can be observed in metal nanocrystal dielectric composites. Sequential implantation techniques have been developed to form intermetallic nanocrystals and metal core metal shell coated particles in dielectrics. These experiements have resulted in the formation of unique new nonlinear materials that offer new avenues to control and enhance the optical properties by changing the strength and center wavelength of the plasmon resonance.

The nonlinear optical behavior of these nanocrystals — such as response time, bandwidth and wavelength dependence - have been correlated with the physical characteristics of the nanocrystals. Nonlinear optical measurements show a third-order nonlinearity $\chi^{(3)}$ of order 10^{-8} esu which is strongly enhanced in the vicinity of the plasmon resonance and is is comparable to the best values obtained for semiconductor nanocrystals in glass, while having a substantially shorter relaxation time.. The temporal response time is less than 25 ps, indicating a Kerr-type electronic nonlinear response rather than a thermo-optic effect. The dephasing (coherence) lifetime is less than 100 fs.

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Picosecond Optical Bistability in Metal Nanocrystal Composites Made by Ion Implantation

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1. Motivation and Objectives

Michael Faraday was apparently the first to suggest that the beautiful colors of stained glasses were due to the optical properties of metallic nanoparticles suspended in the glass.[1] Metallic and semiconducting nanoparticles are now used in passive optical elements such as polarizers and filter glasses. The first experiments on the nonlinear optical properties of metal [2] and semiconductor[3] nanocrystals, on the other hand, are of recent vintage. Driven by the interest in synthesizing materials for all-optical switching and computing applications, there has been an explosion of activity in the last decade in nanocrystal composites prepared by low-temperature processing methods (such as sol-gel); film deposition (*e.g.*, metallorganic chemical vapor deposition); physical techniques, such as ion implantation and pulsed laser deposition; and microlithographic techniques. Increasingly, these efforts have been directed at preparing materials suitable for deployment in waveguide devices, especially in thin-film geometries.

In our 1993 proposal to the ARO, we stated that "the objectives of the proposed research are (1) to develop processing techniques to control the size and size distribution of metal nanoclusters; and (2) to discover correlations between the nonlinear optical properties of the materials and their processing history. The ultimate objective is to predict and control materials properties based on desired nonlinear optical performance. We propose to test three key hypotheses:

- that metal clusters of varying useful sizes and size distributions can be produced by ion implantation with subsequent thermal and/or laser annealing and laser sizing;
- that the nonlinear optical behavior of these nanoclusters — such as response time, bandwidth and wavelength dependence - are correlated with the physical characteristics of the clusters and are consistent with effective medium theory; and
- that the nanocluster composites created by implantation of noble-metal ions in fused silica represent a new type of nonlinear material with optical properties compatible with photonic device technology."

For the past four years, with the support of the Army Research Office, we have been studying metallic nanocrystal composites, synthesized primarily by ion implantation with suitable post-implantation annealing. As shown in detail in Section 2, we have accomplished all the goals stated in our original proposal, and pursued a number of other important avenues of study which were not obvious to us when the original proposal was written. We have also developed an agenda for future research based on past success which will push the state of the art substantially farther.

2. Technical Accomplishments

The following paragraphs outline the specific accomplishments keyed to the three hypotheses we set out to test in synthesis and nonlinear optical performance.

1. Demonstrate "that metal clusters of varying useful sizes and size distributions can be produced by ion implantation with subsequent thermal andlaser annealing and laser sizing."

a. Established the use of ion implantation and post implantation to form a wide range of elemental metal nanoclusters in high purity dielectrics. One of the past experimental problems in the study of metal nanocluster systems that has limited other groups has been the ability to form elemental nanolcusters with controlled particle size and size distributions in desirable mediums. While past techniques such as ion exchange have been used to form metal nanoclusters, the formation techniques have been limited to metal ions suitable for the ion exchange process and to glasses containing a variety of impurities i.e., soda lime glasses. These impurities usually result in unwanted absorption and effect the kinetics of formation of the nanoclusters. We have succeeded in forming elemental metal nanoclusters of Cr, Mn, Fe, Ag, Cu, Au, Ni, Cd, In, Sn, Sb, Pb, Bi, Ga, Zn Sc, Ti, Si and Ge in high purity silica and Ag and Au in Al_2O_3. Established ion implantation protocols and post processing treatments for which the size and size distribution of the elemental nanoclusters can be controlled. This control has allowed us to correlate the nanocluster microstructure with the optical response and to show that the quantum size effects are present and can be observed in metal nanocluster dielectric composites.

b. Using multi-energy implantations we have succeeded in establishing depth or vertical control over the nanoclusters. In principle this will allow for the building of vertically integrated structures.

c. Used sequential implantation techniques to form intermetallic nanoclusters in dielectrics. These composites have significantly different optical properties than single-element nanocluster composite counterparts. These differences can result in lower absorption and increased nonlinear index of refraction, n_2, resulting in higher figures of merit for these materials. We have shown that with the formation of intermetallic solid solution nanoclusters, the optical properties are modified in ways consistent with effective medium theory.

d. In the process of studying the formation and growth of these metal nanoclusters we have shown that thermodynamics can be applied to small numbers of atoms and can be used to advantage to drive the formation of unique metal quantum dots.

e. Established sequential implantation protocols for modification of the host material by polarizable ions (Ti, Sb, Sc) and subsequent formation of elemental metal nanoclusters. We have shown that the nonlinear response of elemental Au and Ag nanoclusters away from the surface plasmon resonance can be increased. Absorption losses away form the SPR are expected to be much less than near the SPR frequencies. While the n_2 away from the SPR will be lower due to lack of local field enhancements, the significantly lower linear and nonlinear absorption can result in a higher overall figure of merit for these materials. The optical properties of elemental metal nanoclusters can be affected by the presence of polarizable ions incorporated into the silica host. The presence of polarizable transition metal ions leads to enhancements in the nonlinear response of metal nanoclusters off the SPR frequency. Using sequential implantation of polarizable ions and metal colloid forming ions we have demonstrated it is possible to shift the frequency of the surface plasmon resonance of the metal colloids and significantly increase their nonlinear response. The presence of these ions also lead to changes in the formation kinetics of the metal nanoclusters.

2. Demonstrate "that the nonlinear optical behavior of these nanoclusters — such as response time, bandwidth and wavelength dependence - are correlated with the physical characteristics of the clusters and are consistent with effective medium theory."

a. Nonlinear optical measurements show a third-order nonlinearity $\chi^{(3)}$ of order 10^{-8} esu which is strongly enhanced in the vicinity of the plasmon resonance. The temporal response time is less than 25 ps, indicating a Kerr-type electronic nonlinear response rather than a thermo-optic effect.

b. Measurements of the nonlinear absorption for this first generation of coated nanocrystals showing that control of the ratio of the two elements in an intermetallic .

c. Working in planar geometries, we have shown that the intraband quantum-confined optical transitions show the predicted $1/r^3$ enhancement as the cluster radius r is decreased by controlling the growth of nanocrystals during implantation.

d. In the case of Ag nanocrystals embedded in soda-lime glass, we showed that laser irradiation at high intensities can lead to photochemical oxidation of the nanocrystals and that this, in turn, produces dramatic, irreversible changes in the sign and magnitude of the nonlinear index of refraction.

e. For Cu nanocrystals in SiO_2, we showed that altering the chemical composition of the substrate by implanting fluorine can have dramatic effects on the relaxation rates of the composite material when irradiated with picosecond laser pulses, due to the incorporation of the fluorine ions into the silica network and the subsequent lowering of the thermal conductivity. The accompanying change in the absorption properties from nonlinear absorption to nonlinear saturation indicates that nonlinear optical spectroscopy of the nanocrystals can, in principle, be used as a sensitive probe of interface properties in these nanocomposites.

3. Show "that the nanocluster composites created by implantation of noble-metal ions in fused silica represent a new type of nonlinear material with optical properties compatible with photonic device technology."

a. We demonstrated that high volume fraction of metal ions can be incorporated in sapphire and in high purity silica without the presence of glass modifiers to stabilize against the devitrification of the sapphire or silica.

b. We showed that use of sequential implantation to produce intermetallic alloys and metal core metal shell coated particles in dielectrics represents the formation of unique new nonlinear materials that offer new avenues to control and enhance the optical properties of these materials by changing the strength and center wavelength of the plasmon resonance. In particular, Ag/Cu metal core/metal shell nanocrystals show a gain in one important figure-of-merit due to increases in the nonlinear index coupled to a decrease in nonlinear absorption.

c. Nonlinear optical measurements show that the nonlinear index of refraction is comparable to the best values obtained for semiconductor nanocrystals in glass, while having a substantially shorter relaxation time. The dephasing (coherence) lifetime is less than 100 fs.

d. Implantation protocols are variations of techniques presently used in present research and industrial practice. Most of our work was accomplished with accelerators similar to those used in industry.

3. Graduate students supported

During the period of the grant, one student has completed Ph.D. dissertations, one has completed an M.S. degree, and several others have received partial support, for example, during summer work. **Li Yang** (Ph.D., 1993) was the pioneer student on the nonlinear optical studies of these materials. She is now a senior research associate in the Department of Physics at Cornell University. **Toby Anderson** who expects to receive his Ph.D. in 1998 has focused on synthesis and optical and microscopic characterization of nanocrystal composites. **Danny Osborne**, who has passed the Ph.D. qualifying examination and expects to receive the Ph.D. in 1998, has been a co-author on a number of publications in nonlinear optics. **CPT John D. Hamilton**, an officer in the Regular Army who will be posted to the United States Military Academy as an instructor in the Department of Physics beginning in July 1997, took the lead role in the developing the pulsed-laser-deposition facility now being used to synthesize film-based nanostructure composites.

The inherent interest in this project has also attracted undergraduate students, generally supported by other funds, who have been involved in the research and have contributed to publications. Frederick M. Smith (Vanderbilt '94), now attending Carnegie-Mellon University on a National Defense Education Graduate Fellowship worked in the Haglund group during 1993-1994 and was co-author of one of our most important papers demonstrating the quantum-size effect. Gene Woo Lee, holder of a prestigious McMinn Scholarship at Vanderbilt and now in graduate school at the University of Illinois, used his McMinn research funds to work in the group during the summer of 1996; he will be a coauthor on one of our forthcoming papers on laser annealing of metal nanocrystal composites.

4. Publications acknowledging ARO support

A. Archival Publications

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20. "Optical Properties of Multi-component Antimony-Silver Nanoclusters Formed in Silica by Sequential Ion Implantation", R.A. Zuhr, R.H. Magruder, III and T.S. Anderson, Mat. Res. Soc. Symp Proc., 396 (1996) 391-396.

21. " Ion Beam Synthesis of Nanocrystals and Quantum Dots in Optical Materials", C.W. White, J. B. Budai, S.P. Withrow, J.G. Zhu, S.J. Pennycook, R.H. Magruder, III and D.O. Henderson, Proceedings of the International Conference on Ion Implantation Technology, 824-827 (1997).

22. "Formation and Optical Properties of Metal Nanocluster Composites Formed by Sequential Ion Implantation of Cd and Ag", R. A. Zuhr, R. H. Magruder, III, and T. S. Anderson., Mat. Res. Soc. Symp A. vol. 438 (1997) 411-416.

23. "Linear and Nonlinear Optical Properties of Metal Nanocluster-Silica Composites Formed by Implantation of Sb in High Purity Silica", R. H. Magruder,III, R.A. Weeks, T.S. Anderson and R. A. Zuhr, Mat. Res. Soc. Symp A. Proc. 438 (1997) 429-434.

C. Invited talks at international conferences and workshops

"Mesoscale Engineering of Nanocomposite Nonlinear Optical Materials," Symposium KK Materials Research Society Fall Meeting, Boston, MA, December 1997.

"Using Laser and Particle Beams to Control the Synthesis and Nonlinear Optical Response of Metal-Quantum-Dot Nanostructures," Symposium on "Laser Applications in Microelectronic and Optoelectronic Manufacturing," Photonics West Conference, San Jose, CA, February 1997.

"Information Technology in Advanced Materials Science Education," Symposium JJ, Materials Research Society Fall Meeting, Boston, MA, December 1996.

"Metal Quantum Dot Composites as Nonlinear Waveguide Materials," International Symposium on the Science and Technology of Atomically Engineered Materials, Richmond, VA, October 30-November 4, 1995.

"Formation of Nonlinear Optical materials by Ion Implantation", Optical Society of America, Photosensitivity and Quadratic Nonlinearity in Glass Waveguides, Portland Oregon, September 1995.

"Nonlinear Optical Properties of Metal Quantum-Dot Composite Materials," Conference on the Physics of Materials of the National Research Council of Italy, Naples, Italy, May 1995.

"Laser and Ion-Beam Induced Formation and Modification of Metal Nanocrystal Composites," invited talk in Symposium A, Materials Research Society, Boston, MA, November 1994.

"Third-Order Nonlinear Optical Probes of Interface Dynamics in Granular Nanocomposite Materials," Heraeus Seminar on Nonlinear Spectroscopy of Surfaces and Interfaces, Kassel, Germany, May 30-June 1, 1994.

"Nonlinear Optical Properties of Metal Quantum Dots Synthesized by Ion Implantation," symposium A (Ion-Beam Processing of Materials), Fall Meeting of the Materials Research Society, Boston, MA, November 30, 1993.

"Optical Properties of Small Metal Clusters Formed in Silica By Ion Implantation", Gordon Research Conference on Optical Phenomena in Glass, The Tilton School, July 1992.

"Nonlinear Optical Properties of Metal Nanocrystal Composites made by Ion Implantation," Gordon Research Conference on Particle-Solid Interactions, Holderness Academy, July 1992.

"Third-Order Optical Nonlinearities in Metal-Cluster-Composities Made by Ion Implantation," Glass Embryo Group of the New Glass Forum, Japan Ceramic Society, May 1992.

5. Collaborations

We have benefitted in this project from significant external collaborations. We have enjoyed a long standing and continuing collaboration with Dr. Ray Zuhr and Dr. Woody White of the Surface Modification and Charaterization Facility at Oak Ridge National Laboratory. We also have an ongoing collaboration with S.H. Morgan of Fisk University.

Two NATO travel grants, one to Prof. Magruder and the other to Prof. Haglund, have made possible joint research with the University of Sussex in England and with the University of Padua in Italy, where Paolo Mazzoldi and his group are exploring combinations of ion exchange and ion implantation to produce cm^2 areas of microns deep nanocrystal-loaded waveguides. A summer cooperative research grant from the Southeastern Universities Research Association made possible our initial exploration of pulsed-laser deposition in collaboration with Dr. Douglas Lowndes of the Oak Ridge National Laboratory. A recent collaboration between Prof. Haglund and Dr. Carmen Afonso in the Instituto de Optica, CSIC-Madrid, has given us the opportunity to study the nonlinear optical behavior of multilayer structures containing Cu nanocrystals in polycrystalline alumina.

References

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2. Ricard, D., Roussignol, Ph. and Flytzanis, Chr., 1985. "Surface-mediated enhancement of optical phase conjugation in metal colloids," Opt. Lett. **10** (10), 511-513.

3. Jain, R. K. and Lind, R. C., 1983. "Degenerate four-wave mixing in semiconductor-doped glasses," J. Opt. Soc. Am. **73** (5), 647-653.